

Twin Knudsen Cell Configuration for Activity Measurements by Mass Spectrometry

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ABSTRACT

A twin Knudsen cell apparatus for alloy activity measurements by mass spectrometry is described. Two Knudsen cells—one containing an alloy and one containing a pure component—are mounted on a single flange and translated into the sampling region via a motorized x - y table. Mixing of the molecular beams from the cells is minimized by a novel system of shutters. Activity measurements were taken on two well-characterized alloys to verify the operation of the system. Silver activity measurements are reported for Ag-Cu alloys and aluminum activity measurements are reported for Fe-Al alloys. The temperature dependence of activity for a 0.474 mol fraction Al-Fe alloy gives a partial molar heat of aluminum. Measurements taken with the twin cell show good agreement with literature values for these alloys.

Index Entries: Double Knudsen cell configuration; mass spectrometry; activity measurements.

INTRODUCTION

One of the most valuable applications of Knudsen Cell Mass Spectrometry (KCMS) is the direct determination of alloy activities. This is done by measuring the ion intensity of a component A in the alloy and comparing it to the ion intensity of that of component A as a pure compound. Consider an alloy AB in a Knudsen Cell Mass Spectrometer; the activity of A at a temperature T is given by:

$$a_A(x_A) = (P_A(x_A)/P_A^\circ) = \{[kI_A(x_A)T]/[\sigma]\} / \{[k'I_A^\circ T]/[\sigma]\} = [kI_A(x_A)]/[k'I_A^\circ] \quad (1)$$

Here a_A is the activity of component A , $P_A(x_A)$ is the vapor pressure of component A at mole fraction x_A , and P_A° is the vapor pressure of the pure component A . Following the pressures are the correlation between ion intensity and pressure— $I_A(x_A)$ is the ion intensity of component A at x_A , I_A° is the ion intensity of the pure component A , k and k' are calibration constants, T is the absolute temperature, and σ is the ionization cross-section. The temperatures and ionization cross-sections cancel for measurements taken on the same species and at the same temperature.

There are several studies in the literature based on this technique (2–4). These studies involve heating a pure specimen or standard, taking a measurement, cooling, changing the specimen, and heating the alloy and taking a second measurement. It is essential that k and k' are the same for the two measurement steps. This can be accomplished by accurate alignment of the cell and mass spectrometer and, if possible, maintaining current to the mass spectrometer filament, focusing plates, and multiplier for added stability when changing the specimen.

However, most high temperature mass spectrometers cannot maintain a constant calibration constant from run to run. Alignment of the cell may vary and characteristics of the ionizer may vary, leading to a difference in the calibration constant of $\pm 10\%$. Thus, another approach must be taken to obtain precise activity measurements.

These approaches have been discussed by Raychaudhuri and Stafford (5a) and Kato (5b) and will only be briefly summarized here. Perhaps the most common is the “ion-current ratio” technique developed by Belton and Fruehan (6) and Neckel and Wagner (7). This technique has been used successfully for a number of binary metallic alloys and even some ternary metallic alloys (8). It involves measuring the ion intensities of both components and taking their ratios, which effectively cancels calibration constants. Even the ionization cross-sections are unnecessary. Then a modification of the Gibbs-Duhem equation is used to obtain the alloy activities. This technique has two requirements: the vapor pressures of the alloy constituents must be measurable over the entire composition range; and a wide composition range of alloys must be examined in order to perform the Gibbs-Duhem integration. However, many alloys may contain constituents with widely differing vapor pressures (e.g., Ni-Al). Also, it may not always be possible to examine a wide composition range of alloys.

A third method for determining activities is the “dimer-monomer method,” which involves using both the monomer and dimer vapor pressures to solve for activities. This leads to two equations with two unknowns (i.e., the activity and the machine constant), and thus activity can be determined (5,9). However, this depends on the system having a vapor composition with monomers and dimers in measurable quantities, which is not always the case.

Recently, a "valved Knudsen cell" system was reported (10), which allows alloying element additions from outside the system and the subsequent change in activity to be measured. This elegant approach allows numerous alloy compositions to be studied in one experiment with a single cell. However, it is suitable only for liquid alloys so that complete mixing occurs each time the additional component is added.

The most versatile approach to measuring alloy activities is with an internal calibration cell in a multiple Knudsen cell configuration. Such an approach was first developed by Buchler and Stauffer (11) and has been modified by several other investigators (12–15). By putting a standard in one cell, sampling from it, and then moving to the alloy, one can obtain a rapid and direct measurement of alloy activity. There are, of course, a number of important considerations in the construction of such a system. Both cells must be at the exact same temperature and it must be possible to position each cell in exactly the same place. There can be no mixing between the molecular beams emerging from the two cells. These problems have been solved in a variety of ways. Generally, one large furnace is used for both cells. Some type of vacuum motion controller is used to position the cells. Some investigators have used a pseudolinear motion controller (14), others have used a rotary motion controller (12).

Molecular beam mixing is perhaps the most formidable issue. Buchler and Stauffer (11), Johnson and Burley (12), and Camerisi et al. (13) appear to have enough separation of the cells and beam collimation to prevent this. Chatillon et al. (14) have developed an elegant approach centered on a series of small apertures so that the ionizer effectively sees only the inside of the cell. This arrangement limits contributions from beam mixing and heat-shield re-evaporations. Stickney et al. (15) have attached tubes to the orifices of the Knudsen cells. In this case, care must be taken to avoid interactions with the tube walls.

The purpose of this work is to describe our twin Knudsen cell apparatus. We have used a system of shutters adjacent to the cells to prevent beam mixing. Measurement of activities in Cu-Ag and Fe-Al alloys will be presented to illustrate the technique.

EXPERIMENTAL

The mass spectrometer was a 90° magnetic sector instrument configured so that the molecular beam, ionizing electrons, and ion beam were all mutually perpendicular (model 12-90-HT, Premier American Technologies Corp., formerly MAAS/Nuclide, Bellefonte, PA). Such a configuration allows for direct sighting with the pyrometer telescope into the Knudsen cell orifice, which allows precise temperature measurement and alignment of the cell. This system is shown schematically in Fig. 1. The shutter between the ionizer and the Knudsen cell chamber can select either a 1-mm slit or a 5-mm round hole. For these experiments the 5-mm hole was selected, which allows clear sighting of the cell.

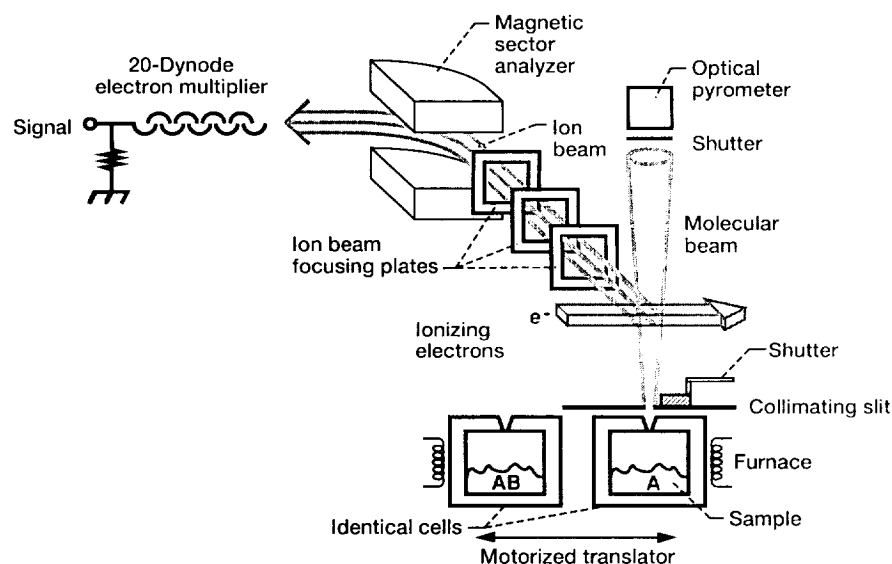


Fig. 1. Schematic of mass spectrometer with double Knudsen cell attachment.

The Knudsen cell flange is shown in Fig. 2. Heating was accomplished by a tantalum element with a "continuous hairpin" design. This was fabricated from 0.32-cm tantalum rod and was found to give a near zero temperature gradient for a single cell. A standard low-voltage, high-current power supply was used for heating. Temperatures were set by controlling the voltage and measuring with a pyrometer; no feedback loop was used. The two Knudsen cells were mounted in a tantalum block that tended to minimize both vertical temperature gradients through each cell and horizontal temperature gradients between the two cells. The actual Knudsen cells were 0.95 cm in diameter \times 2 cm high and had a cylindrical orifice of 0.77 mm diameter \times 1.7 mm. Cells were fabricated from graphite, alumina, and zirconia.

As mentioned, temperature was measured from the top into the orifice with a disappearing filament type optical pyrometer (Pyrometer Instrument Co., Northvale, NJ). It was found that certain distances did not allow the pyrometer filament to cleanly disappear. This was owing to a diffraction effect, introduced by sighting through the small apertures (16). A prism allowed the pyrometer to be set at a distance of about 36 in. from the cell top, which gave a cleanly disappearing filament. At 1473 K, the temperature between cells differed by 3 K or less. Temperatures were calibrated by ramping the temperature through the melting point of silver or copper. The first point in an arrest in the ion intensity from the metal indicated the onset of melting. Thus, the temperature correction from the pyrometer reading was determined to be 12 K, which included corrections for the prism and viewport.

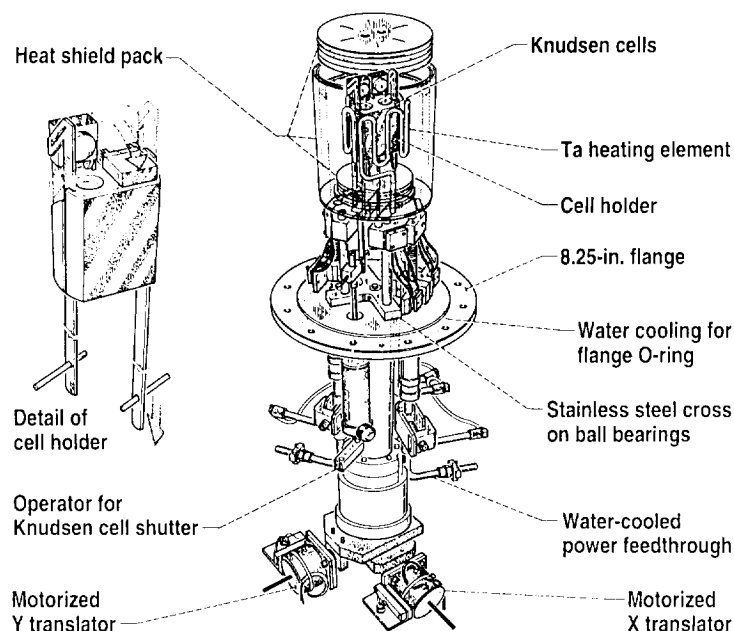


Fig. 2. Schematic of double cell flange, showing detail of cell holder.

The entire cell and furnace assembly was mounted on the stainless steel cross shown in Fig. 2. At the center of this cross was a 1/2-in. rigid stainless steel tube that attached to a commercial X-Y vacuum motion feedthrough (MDC, Hayward, CA). Thus the X-Y translators moved the rod which in turn moved the cross and furnace/cell assembly. One problem with this approach is the length of the tube, which gives some play in the motion of the cross. However, a long rod was necessary to accommodate the water-cooled power feedthroughs. Despite the play, the cells could easily be moved in and out of position. The X-Y translator was further modified with stepper motors and a "joystick" controller. Position was indicated with linear potentiometers attached to the x-y motion feedthrough and wired to digital meters. The pyrometer telescope provided a visual observation of a cell as it was moved into position. It was found that the cells could be reproducibly moved into the same position, since the same ion intensities were obtained on moving the same cell in and out of position several times. In order to water cool the copper block that connected to the Ta heating element and translated with the cells, the power feedthroughs had a section of flexible stainless-steel bellows on them, as shown in Fig. 2. Since the stainless steel cannot carry the large currents to the heating element, flexible copper braids in parallel to the stainless-steel bellows were used. This approach has been used on commercial machines that have limited motion control of a high temperature furnace (Premier American Technologies Corp.).

Mixing of molecular beams from the cells was minimized by the use of shutters over the cells, as shown in the detail in Fig. 2. The Ta block contained Ta cell covers that could be opened via "push-pull" motion controllers from the outside of the vacuum system. The design shown in the detail of Fig. 2 allowed positive opening and closing of the cell covers. The moving parts were lubricated with a suspension of graphite in isopropyl alcohol. At high temperatures, the alcohol vaporized, leaving behind the graphite that left the parts running smoothly. In order to test for mixing between the molecular beams, cell 1 was loaded with Ag and cell 2 was kept empty. The Ag signal emerging from cell 2 (cell 2 cover opened; cell 1 cover closed) was about 2% of that from cell 1 (cell 1 cover opened; cell 2 cover closed). This may be caused by leakage around the cell cover. For activities ≤ 0.10 , this crossover correction should be applied. To measure very low activities (i.e., <0.01), it would be necessary to use another standard and calculate the machine constant, k . Then the ionization cross-section and multiplier gain difference could be applied to calculate the vapor pressure of the alloy component. This then could be used with the vapor pressure of the pure component to calculate the low activity.

As in all mass spectrometer measurements, separation of the signal from background was an important issue. Our magnetic sector instrument was set at a resolution of about 1200, which separated the hydrocarbon peak from the inorganic peak. In a typical experiment, the shutter on the collimating slit (Fig. 1) was left open. The actual measurement was taken as the difference between the cell shutter opened and the cell shutter closed. Ionization was accomplished by electron impact with electrons at 18 eV and 1 Ma total emission current. Detection was accomplished by a 20 dynode electron multiplier at a gain of 10^5 and analog measurement of ion currents. After about five runs, empty cells were placed in the system and the system was heated to a high temperature to bake out any deposits.

RESULTS AND DISCUSSION

Two alloy systems were examined to illustrate the operation of this system. There are literature data available for both Ag-Cu and Fe-Al alloys. Typically, the alloy was allowed to equilibrate at temperature for 1 h or more. Several measurements were taken and the arithmetic mean calculated.

The Ag-Cu alloys were prepared *in situ* with high purity (99.999) Cu and Ag turnings or shot. Graphite cells were used. A silver standard was used and silver activity measured. The mixture was heated above the melting point of copper for about 5 min and then cooled to 1310 K for the measurement. As indicated, it then was allowed to equilibrate for 1 h or more. At 1310 K, ion intensities near the upper limit of the instrument were measured. The literature data(10,17) are at temperatures of 1400 K or higher. For this reason, the literature was extrapolated to 1310 K for comparison to our data via the equation:

Table 1
Measured Activities in Ag-Cu Alloys at 1310 K as Compared
to Extrapolated Literature Values

Alloy composition x(Ag)	a(Ag)–this study ^a	$\Delta H(\text{Ag})$ – Hultgren et al. (17) kJ/mol	Extrapolated a(Ag)–Hultgren et al. (17)	Extrapolated a(Ag)– Howard (10)
0.150	0.391 \pm 0.001	11966	0.387	0.358
0.373	0.616 \pm 0.012	6778	0.634	0.606
0.610	0.752 \pm 0.017	3310	0.742	0.744
0.789	0.821 \pm 0.016	1155	0.842	0.836

^aErrors are $\pm 1 \sigma$.

Table 2
Measured a(Al) at 1410 K in Fe-Al Alloys as Compared
to Extrapolated Literature Values

Alloy composition, Al	a(Al)–this study ^a	$\Delta H(\text{Al})$ – Eldridge and Komarek (19), kJ/mol	a(Al)– Eldridge and Komarek (19)	$\Delta H(\text{Al})$ – Radcliffe et al. (18), kJ/mol	a(Al)– Radcliffe et al. (18)
0.185	0.011 \pm .001	–86,609	0.010	–79,914	0.007
0.341	0.042 \pm .016	–69,036	0.025	–76,149	0.065
0.474	0.112	–53,764	0.099	–58,944	0.113
0.580	0.255 \pm .005	–47,698	0.223	–44,769	0.230

^aErrors are $\pm 1 \sigma$.

$$\ln[a_{\text{Ag}}(T_2)]/a_{\text{Ag}}(T_1)] = (\Delta \bar{H}_{\text{Ag}})/(R)[(1/T_2) - (1/T_1)] \quad (2)$$

Here $a_{\text{Ag}}(T_2)$ is the activity of Ag at temperature T_2 , $a_{\text{Ag}}(T_1)$ is the activity of Ag at temperature T_1 , $\Delta \bar{H}_{\text{Ag}}$ is the partial molar heat of aluminum, and R is the gas constant. The partial molar heats for Ag were taken from Hultgren et al. (17) and interpolated for the particular alloy composition.

There are a number of investigations in the literature of Ag-Cu alloys. These have been discussed by Howard (10) in his recent paper. Table 1 compares our data to extrapolated data of Howard (10) and extrapolated data from the compendium of Hultgren et al. (17). In general agreement is quite good.

Another series of measurements was taken on Fe-Al alloys. These were cast in a separate furnace and solid alloys were studied at a temperature of 1410 K. An aluminum standard was used and aluminum activities were measured. There are several studies of this system in the literature (18–20). Table 2 shows a comparison of the literature values extrapolated to 1410 K and the values measured at that temperature in

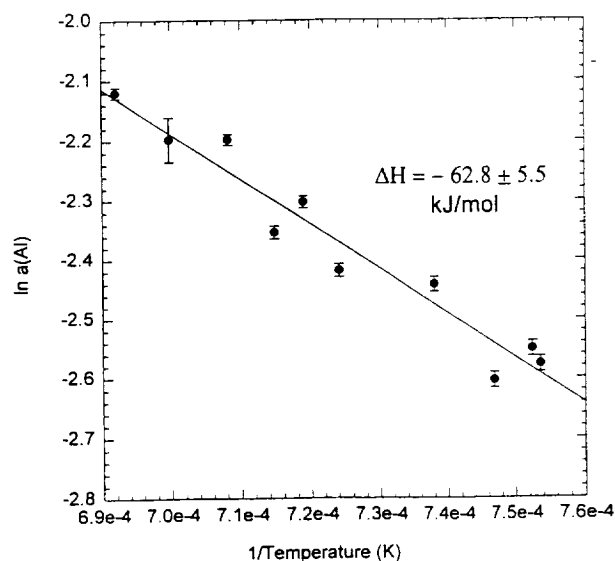


Fig. 3. Plot of $\ln a(\text{Al})$ at $x = 0.474$ vs $1/T$ for partial molar heat of aluminum determination.

this study. The aluminum partial molar heats were taken directly from Eldridge and Komarek (18); Radcliffe et al. (19) report only integral free energies. In this case, the integral free-energy curve was constructed and the partial molar heats were calculated from the tangent intercepts (20). In general the aluminum activity measurements taken with the double cell show good agreement with the extrapolated measurements of other investigators. The measurement at $x(\text{Al}) = 0.185$ could be corrected for the 2% crossover value, as described in the experimental section. Thus, it becomes even closer to the literature values. The measurement at $x = 0.580$ shows some difference from the literature values. This run was repeated several times and the results were quite consistent. The differences may be owing to the extrapolation under these conditions.

From Eq. (2), if activity is known at several temperatures, it is possible to determine a partial molar heat. A plot is shown in Fig. 3. The partial molar heat was calculated to be -62.8 ± 5.5 kJ/mol, which is in reasonable agreement with the heats measured by other investigators, as shown in Table 2.

SUMMARY AND CONCLUSIONS

A twin Knudsen cell apparatus for measuring alloy activities has been described. Two Knudsen cells are mounted on a flange adjacent to each other and moved into the sampling region via a motorized x - y translator. The cells are heated together with a Ta-resistance heating element. The most formidable experimental problem is mixing of the molec-

ular beams from the two cells. This was minimized with a novel system of shutters that could be operated at temperature from the outside of the flange. Measurements were taken of silver activity in Ag-Cu alloys and aluminum activity in Fe-Al alloys. In addition, a partial molar heat of aluminum for 0.474 mol fraction Al-Fe was measured. The measurements from the twin cell system showed good agreement with the literature values.

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